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CHARACTERIZATION OF RARITAN BAY WATERS

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Chicago, Illinois

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Report To
Department of Health, Education and Welfare
Raritan Bay Project
Metuchen, New Jersey

Attn: Paul DeFuleo Jr.

CHARACTERIZATION

OF

RARITAN BAY WATERS

Submitted by
Walter C. McCrone Associates
Chicago 16, Illinois

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CHARACTERIZATION OF NANTAN BAY WATERS

1. INTRODUCTION

In criminalistics work, it is recognized now that a person at the scene of a crime leaves there some particles (fibers, dandruff, hair or etc.) from his person and picks up from there some other particles (soil particles, fibers, pollens, or etc.) characteristic of that scene. By careful examination of vacuum cleaner dust from the scene of the crime and the guilty individual definite and dependable evidence can be obtained linking the individual to the scene of the crime.

In an exactly analogous manner, a river flowing through any area of country or city picks up particulates characteristic of that area and leaves behind particulates characteristic of its earlier history. These particulates will accumulate from five main sources:

1. Mineral particles (sand, clays, other silicates, carbonates sulfates, oxides, sulfides)
2. Sewage
3. Industrial wastes
4. Atmospheric particulates settling on the river or brought to the river by run-off after rains
5. Biological life (protozoa, in particular)

Each one of these particulates can be identified by a trained microanalyst using the microscope and other microanalytical tools. The number and types of particles found at any given point fully characterize that body of water at that point. Because of the tremendous variety of compounds found in any sample of water and because some of these will always be unique to that source it follows that each river can be uniquely characterized. If the "unique characteristics" do not settle out or become chemically altered to non-unique materials then these unique compounds serve as tags for the identification of water from that particular source.

The present problem can be defined as follows: How could we recognize those the water leaving particles the lower harbor (Raritan Bay)? The water in the upper harbor comes from a number of individual sources, among which the major sources (Figure 1) are:

I [illegible] River
J [illegible] River
L [illegible] River
M [illegible] River
N [illegible] River
A [illegible] River
B Arthur Kill
H Passaic Valley trunk system

From an analytical point of view it is necessary to characterize the particulates in each of these sources as well as Raritan bay water to find the appropriate tags. If, for example, the Hudson river contains suspended particles of rutile because of deposits of this mineral upstream and if particles of that mineral are absent from the other sources then the presence of rutile in Raritan Bay tells us that water from the Hudson River enters the Bay. Similarly with each of the other major sources. Each should have one or more tags and monitoring for that substance "downstream" should tell where these waters go.

Once the basic work is completed such determinations should be quite simple since the analyst can look only for particles having specific known characteristics; the large preponderance of other particles can be ignored. Unfortunately, in the preliminary work some of the hundreds of compounds present can be ignored. Each must be evaluated as a possible tag.

II. MICROANALYTICAL PROCEDURES

Of the particulates present in water two types are sufficiently distinctive to be readily identified: protozoa and crystalline substances. It is probable that the present problem could be solved by studying either of these two types of particulates.

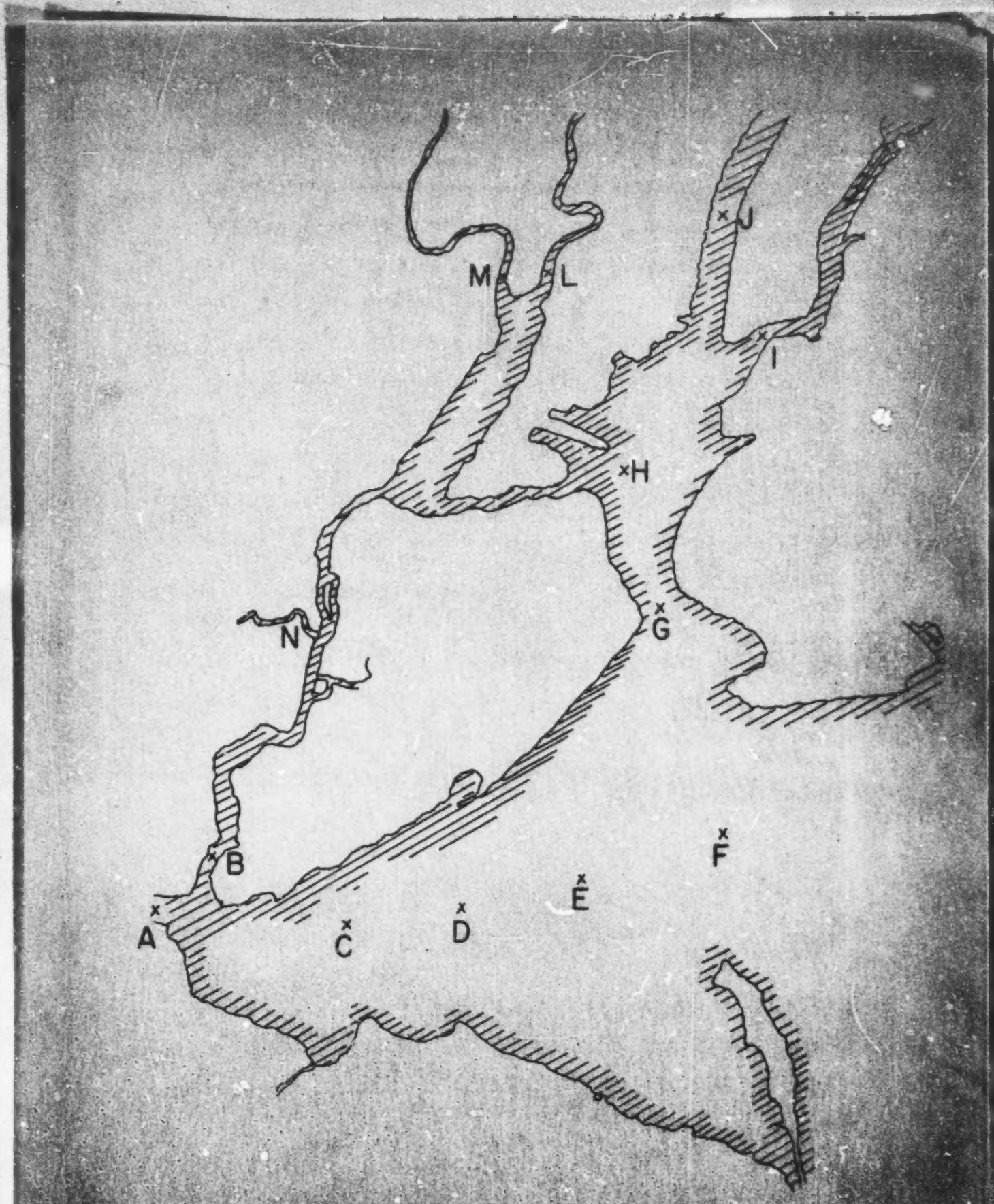


Figure 1. Location of Sampling Points

[illegible] as minerals or industrial wastes.

The study of crystalline substances is carried out by diffraction methods and microscopy. These two methods supplement each other and together are able to identify almost any crystalline substance even when the amount of sample is very small, often less than 1 microgram (10^{-6} grams).

X-ray or electron diffraction is used to study the characteristics of the crystal lattice. The measurements possible on a diffraction pattern uniquely characterize any crystalline substance. The usual measurements are made on a so-called powder pattern. This is a pattern made up of diffracted spots from individual crystals which combining with similar spots from other crystals of that substance form lines at measureable intervals. These lines registered on a photographic film can be measured to give line positions and intensities. Figure 2 shows such a pattern for olivine, a common silicate mineral, along with the data measured from that pattern.

Each crystalline substance has many diffraction lines and mixtures of more than one substance show a pattern made up of all the lines of all substances present. The components of a mixture can usually be identified in a straight-forward though time-consuming procedure. As each component is identified the diffraction lines known to be characteristic of that component are subtracted from the diffraction pattern and one continues until all lines have been assigned.

X-ray diffraction will give diffraction lines only for the major components of a mixture. Components present to the extent of less than about 5% will not usually be detected.

The microscope will also identify small particles and in smaller samples and smaller percentages than x-ray diffraction. A single particle a few microns in diameter and weighing less than 10^{-11} g. can often be identified in a mixture with

d.	Relative Intensities
5.1	15
3.9	20
3.64	35
3.70	15
3.48	30
3.14	30
2.96	20
2.91	10
2.85	20
2.80	20
2.74	80
2.50	100
2.45	100
2.34	10
2.26	50
2.34	30
2.15	30
2.10	5
2.03	5
1.96	10
1.875	10
1.745	100
1.670	20
1.635	20
1.625	20
1.570	15
1.497	40
1.480	80
1.437	10
1.394	30
1.352	30
1.318	20
1.294	10
1.266	5
1.190	10
1.169	5
1.159	5
1.139	15
1.101	15
1.080	10Ka2
1.037	30
1.022	25

Figure 2. X-Ray Pattern for Olivine

[illegible] of other particles. There are many physical properties of each particle that can be used for characterization and identification using the microscope.

Morphological properties

size
shape
crystal angles
homogeneity
crystal system

Optical properties

transparency
color, by reflected light
color, by transmitted light
reflective indices
optic axial angles
dispersion
birefringence
fluorescence
correlation of optics and morphology

Other properties

solubility
density
melting point
microchemical reactions

These properties are used to identify any substance previously described and for comparison of an unknown with a known. The identification of a complete unknown will be laborious; the recognition of a familiar substance can be very rapid. Quartz, diatoms, wood fibers, pollens, and many other particulate substances can be identified at a glance. As the microanalyst becomes familiar with additional components in a given series of samples he can then identify these components quickly and easily.

III. ANALYTICAL DATA

Both diffraction and microscopy have been used on the series of samples available. It was soon found however, that the filter samples could not be used for microscopy because the organic matter had irreversibly imbedded the various particulates so that even on ashing they could not be studied individually.

The filter samples were used, however, for diffraction by ashing first at a low temperature (under 600°C). Samples were also prepared for both diffraction and microscopy from the suspended samples by a density separation using aqueous solutions

of thallium formate. In this way, most of the organic matter, diatoms, sand and other analytically insignificant substances were removed leaving only the high density components. These samples were x-rayed and then studied microscopically.

The x-ray data for the heavy fractions appear in Appendix A. Similar data for the mixed filter samples are given in Appendix B. Prints of the original x-ray shots of the mixed samples appear in Appendix C and the heavy fraction in Appendix D.

Considerable microscopic work has been done on these samples. Each sample can be easily differentiated from the others by the gross appearance under the polarizing microscope. There are, in fact, so many differences that it will take time to determine which are significant (See photomicrographs in Appendix E). There are, conservatively, more than 1000 chemical substances in these samples. Most are not significant in that they are either common constituents of most water courses (e.g., sand) or they settle, dissolve or react too quickly to act as permanent logs. The microscopic approach is the most appropriate in the long run in terms of dependability, simplicity and speed but, at the start, x-ray diffraction has advantages. The major advantage is, as a matter of fact, related to one of its limitations, the fact that by x-ray diffraction you see only the major constituents (i.e., above 5%).

IV. DISCUSSION OF THE DATA

The most significant data are the diffraction data on the mixed filter samples. This would not have been the case if we had not used too much of our suspended samples in learning the best techniques for separation of the high density fractions. The latter samples are not strictly comparable because of variations in technique. Some run above and some below, quartz on the density scale. Also our technique for separation of the heavy fraction improved with practice and later samples represented better separations. These variations are very bad since we do not know in many cases whether differences between samples are real or due to differences in technique.

Actually, we have sieved and x-rayed the light fractions for each sample and the interpretation could, in time, be achieved.

Because of time limitations for the present study we decided to restrict most of the analytical thinking to the results on the sized filter samples. We did refer many times to the heavy fractions, however, and these helped considerably to confirm identifications made by x-ray diffraction. They also showed how zinc oxide can be present apparently in higher percentages in the lower harbor samples. The microscope showed that these particles (ZnO) are so small they remain suspended after other coalyser particles have settled out.

Table I shows the composition of the thirteen sized filter samples as determined on the x-ray diffraction patterns and confirmed microscopically.

TABLE I
Composition of Suspended Particulates

Source	Percent by Weight						
	Amorphous	Sand	ZnO	Clays	$ZnOCl_2$	$(Zn,Fe)Fe_2O_4$	Unident.
A-Raritan River	10	35	5	20	0	20	40
B-Arthur Kill	15	20	10	10	0	10	35
E-Rahway River	10	10	0	0	0	40	40
H-Passaic River	15	20	5	10	0	15	40
L-Elizabeth River	15	20	0	15	0	10	40
J-Hudson River	25	50	0	20	0	5	25
I -Hint River	15	10	10	5	5	5	50
H-Passaic Val. Tr.	15	15	15	10	0	5	40
G-Narrows	25	15	20	10	5	0	25
C-Raritan Bay(West)	20	25	20	5	20	5	25
D-Raritan Bay	25	25	25	5	5	0	15
E-Raritan Bay	20	20	20	5	0	0	35
F-Raritan Bay(East)	20	20	25	5	0	0	30

V. CONCLUSIONS

These preliminary results show that crystallographic methods (microscopy and diffraction) can identify suspended particulates in rivers and harbors. Given time such analyses could be made much more complete than those given here. One station indicated by this work; more quantitative estimates of the movement of bodies of water

bired on analyses of suspended particulates will have to consider slow solubility (particulates), reactivity (zinc oxide reacting to give basic zinc chloride), and settling rates as they vary with particle size.

So far as the major objective of this work is concerned we do know more than we did about the movement of water into the lower harbor.

Note first the zinc oxide, ZnO, from Table I. This component comes into the area from the Raritan River, the Arthur Kill, the Passaic River, the Passaic Valley Trunk System (all in Jersey) and surprisingly enough from the East River but not the Hudson River. This substance is very finely divided (usually 1 - 8μ) and stays suspended almost indefinitely. It enters the lower harbor both through the Narrows (from the East River and the Passaic Valley Trunk System) and from the West. The percentage of ZnO in the lower harbor is higher than any of the natural sources because most of the coarser particulates settle out in the Bay. Note that sample E in the middle of Raritan Bay contains the least ZnO of the four Bay samples. This is reasonable since some dilution with ocean water as well as some settling would lower the percentage the farther away from the Narrows and the West end of the Bay the sample is taken.

The presence of basic zinc chloride, written $ZnOCl_2$ in Table I, shows this component in large amounts only in the East River, the Narrows and, strangely enough, at first in the West end of Raritan Bay. This means that the zinc oxide entering Raritan Bay from the West has reacted to give the basic salt and this rapidly settles or dissolves on traveling Eastward. Water from the Narrows does not travel into the Bay to a major extent under the conditions preceding the time this sample was taken since no basic zinc chloride is found at F. The zinc oxide figures, however, indicate some movement of Narrows waters into Raritan Bay.

The iron oxide, $(Zn, Ni)Fe_2O_3$, found in most of these samples is also of interest. This substance comes in largest quantity from the Rahway River but in

fair amounts from the Raritan River, Arthur Kill and Hackensack River. Lesser amounts come from the Hudson and East Rivers and from the Passaic Valley System. It may seem strange that none of this substance reaches the Narrows but again the microscope shows us that these particles are 10 - 100μ and should settle out on passing through the upper harbor. Some does, however, get into Raritan Bay but only in the West end.

The data on the clays do not tell us very much since all samples except the Rahway River show about the same percentage of this substance. Potentially however, the clays could be very valuable since they vary considerably in microscopic appearance from deposit to deposit.

Our final conclusion must be that even the preliminary data show differences between the various sources and indicate, at least, that during an ebb tide the lower harbor is fed mostly through the West end and the Narrows water seems to pass mostly out to sea. We are first to suggest caution in the use of these conclusions. Much more work must be carried out before any final conclusions can be drawn.

VI. FUTURE WORK

Before routine analyses can be made of any water samples in the New York area a great deal of careful analytical work must be carried out on a number of samples. Separation methods, probably based on density and perhaps using a density gradient column, must be applied to increase the percentage composition of minor constituents.

Sediment samples from the floor of the Bay will be of great interest and will help to give figures for movement of the waters in that area over longer time periods.

Smaller particles must be studied to eliminate the possibility of incorrect conclusions caused by rapid settling of coarser particles. The electron microscope may well be useful here.

Larger samples must be taken but the particulates must never be allowed to dry out. They may be filtered but should be shipped wet to the laboratory.

VII. FINAL CONCLUSION

Definite progress has been made on the characterization of the individual sources of pollution leading into lower New York harbor and on the movement of these waters on their way to the ocean. Considerable additional analytical work is necessary before the great potential of these methods is achieved. We have no doubts, now, that any body of water in the New York area can be uniquely characterized and followed until it is diluted 100 times or more. We hope to have the opportunity of submitting a detailed proposal covering such a program.

Respectfully submitted,

W. C. McCRONE

APPENDIX A

X-Ray Data for Heavy Fractions

d	I	J	L	M	H	G	A	B	N	C	D	E	F	
11.0								10						
10.5		20												
8.1								10						
7.9	20					15				30	30			$ZnOCl_2$
7.1		5	10		10	2	5		5		5			
6.9	100									95				
6.5								15						
5.40	5									5				
4.95								5						
4.48	5	5	15		20	10	20		20	10	10	10	10	Clay
4.35		10	25		25		30		20					Quartz
4.05	8	5				20	5			5	5	5	5	
3.88		5				5						20	30	$BaSO_4$
3.78													5	$BaSO_4$
3.71	10							20						
3.65			10											
3.55														
3.52										5	5		8	$BaSO_4$
3.35	10	10	20						50	5				
3.31					10		10	10				5		Clay
3.45		10								10	40		70	$BaSO_4$
3.34	30	100	100		100		100		100		30		80	Quartz
3.21		20	20		20		20		20	20				$ZnOCl_2$ / Clay
3.19											5		5	
3.17	35											10		
3.15			15			5								
3.10		20						10		10	10		70	$BaSO_4$
2.96			10		5				20			5		$(ZnOH)Fe_2O_3$
2.94										5				
2.90	15					10				5	5			
2.81										20	20		30	ZnO / $BaSO_4$

APPENDIX A(Cont'd)

d	I	J	L	M	N	G	A	B	M	C	D	E	F	
2.78	100	40			25	20		10	20	70	80		60	$ZnOCl_2$ / $BaSO_4$
2.70			20							20		10		
2.67										40	15			
2.66										20	10			ZnO
2.57	20	[illegible]	20		40	15	20	20	40	10	10	10	10	$ZnOCl_2$ / ZnO
2.52	15	20						10						$ZnNiFeO$
2.48			20		25		15			20	10			ZnO / Quartz
2.44		10	25					10	20		15			
2.38					20			20		15	5	5		$ZnOCl_2$
2.33								10					5	
2.25			20		10				10					Quartz
2.26							15		10					
2.22	10	10	20		5	10			10	15	20		20	$BaSO_4$
2.21														
2.17								10						$BaSO_4$
2.13		15	20		20	10	20		10	20	30		100	Quartz
2.06											5		10	$BaSO_4$
2.02						5					3			
2.00					10			10		10				
1.98			15				10	10						Quartz
1.92	15		10		5			10	10	15	30		5	ZnO
1.885											5		10	$BaSO_4$
1.82	5	20	20		35		20	15	20					Quartz
1.78										5				
1.70	10					5				5	5			$ZnOCl_2$
1.67		5	10		20		8				5		15	$BaSO_4$
1.64		20			25	20			20	20	40			
1.625	20		25					16						ZnO
1.59	20					5				20	10			$ZnOCl_2$
1.55	40	10	25		20	5	20		20	20			10	Quartz
1.51	5	10	10		20	10			20		10	5	5	
1.50							8							

APPENDIX A(Cont'd)

d	J	J	L	M	H	G	A	B	N	C	D	E	F	
1.49			5		20									ZnO
1.48									10					
1.455					20									
1.45		10	10											
1.425						5					5		10	
1.405	5													ZnO
1.375		15	30		20		30	10	10					Quartz
1.29					10									
1.29			5						5					
1.28		15	10				10							
1.205			10		8		5							
1.126		10	10		8		5							
1.145											5		5	
1.045	10	10				5					5			
0.957	10													

APPENDIX B

X-Ray Data for Ashed Filter Samples

d	I	J	L	M	H	G	A	B	N	C	D	E	F	Identity
14.0										5	5	5		
3.80		15						20		5	5	5		Clay
3.2										5	5	5		
3.1		25												
4.50	8	20	8	8	10	8	20	20		10	14	10	8	Clay
4.25	20	25	25	30	20	15	20	20	5	15	15	15	15	SiO_2
4.08	10	5	8	5	8	6				8	4	4	6	
3.90		10												
3.80									5					
3.75				15										
3.50	5	5	5	10	5		10	8	10					Clay
3.38														Clay
3.34	100	100	100	100	100	60	100	100	30	40	50	70	60	SiO_2
3.25									20					NaCl
3.20	15	20	30	20	20	15	20	20		10	10	10	10	Clay
2.96	10	10	15	25	20	5	20	10	10	5		5	5	FeZnNiO
2.82	80			30	60	100	20	30	100	65	60	100	65	ZnO, NaCl
2.70				5										
2.60	60		5	10	50	30	20	25		50	50	40	40	ZnO
2.57		30												
2.54	20		35	50	20		40		20					FeZnNiO
2.48	100	10	15	5	80	50	40	60		100	100	90	100	ZnO, SiO_2
2.40		5												
2.32		5												
2.28	10	10	15	8	10	5	8	5		5	5	5	5	SiO_2
2.24		4	8	3										SiO_2
2.13	8	10	8	8	10	5	10	8		8	8	10	10	SiO_2
2.09				8					10					
1.995									50					NaCl
1.98	5	10	5	20	5	30	5			10	5	20	10	NaCl, SiO_2
1.91	35				15	10	10	10		20	20	20	20	ZnO
1.88				10										

APPENDIX B (Cont'd)

d	I	J	L	M	N	O	A	B	H	C	E	R	F	Identity
1.86									5					
1.83	15	25	20	15	15	10	15	15	20	21	10	10	10	SiO_2
1.74									5					
1.70									15					
1.676	5	5	5		5					5	5	5	5	SiO_2
1.56						5								
1.625	60			15	50	40	20	20	20	40	45	40	35	NaCl, ZnO
1.615			5											
1.545	10	15	20	10	10	5	10	5		5	5	5	5	SiO_2
1.510		5												$MnZnFeO$
1.480	60		15	20	20	20	10	15	10	40	45	20	25	ZnO
1.456		5	5											SiO_2
1.415	5			5	5	10			25	5	7	10	9	
1.370	50	15	25	15	20	20	10	40	5	40	45	20	25	ZnO, SiO_2
1.365	10				10	10				20	20	10	20	
1.365										5	5			SiO_2
1.360						1								SiO_2
1.330					5									SiO_2
1.288		5	5	10		20			35	5		5	5	SiO_2
1.226						5				10	9	5	9	SiO_2
1.266	10	5	5		10						6			SiO_2
1.195	10	5			10	5	10			5	9	5	5	
1.153				10		20			20	4		10	4	NaCl
1.095	10				5	7				15	15	5	15	
1.082			5											
1.035	10					5				5	7	5	5	
1.044	15				5	5				12	17	9	15	
1.016	10					5				9	10	4	10	
0.985						5				5	5	4	4	

I
J
L
H

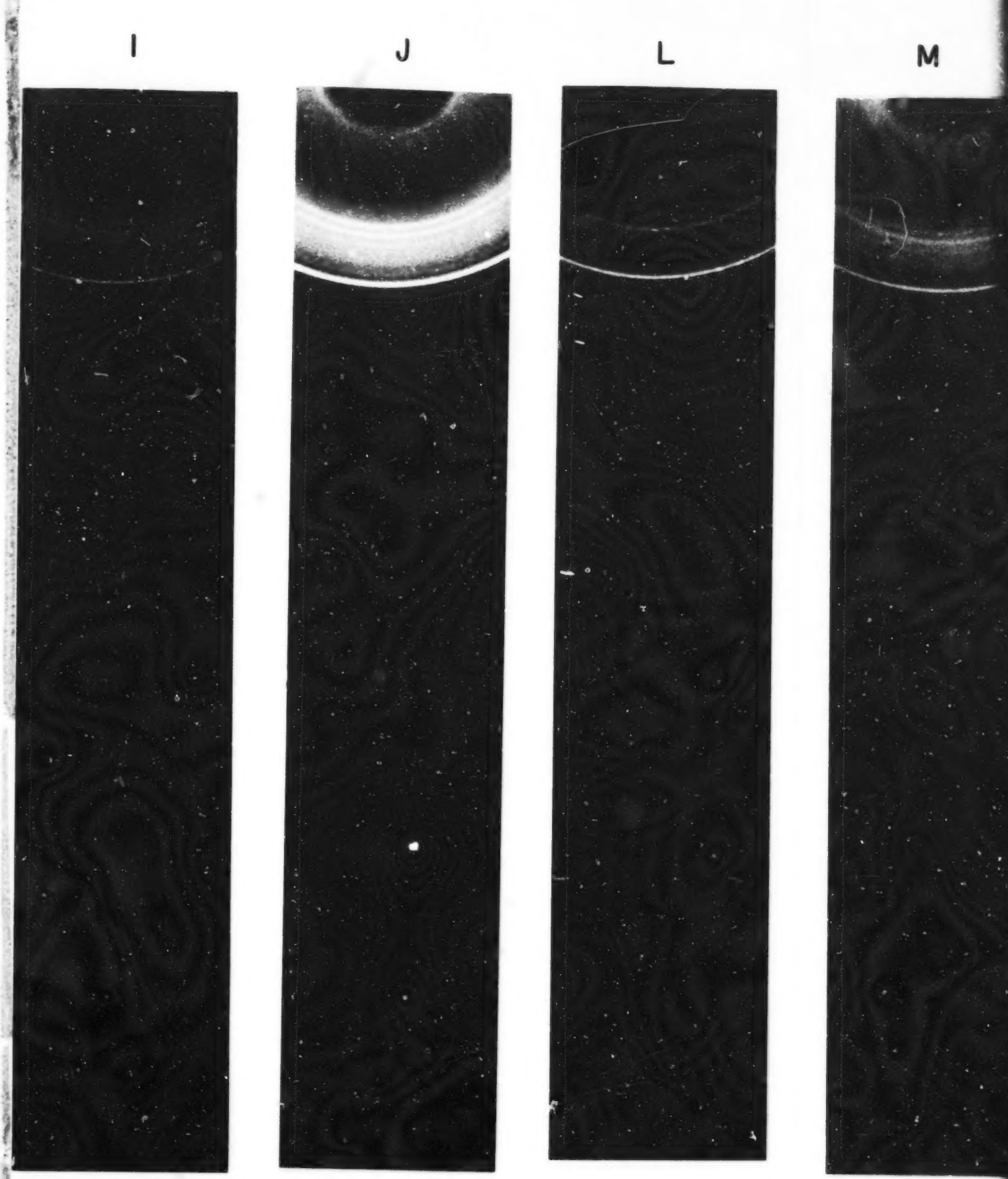
H
G
A
B

N
C
D
E

C
D
E
F

Appendix C

X-ray Data on Heavy Fractions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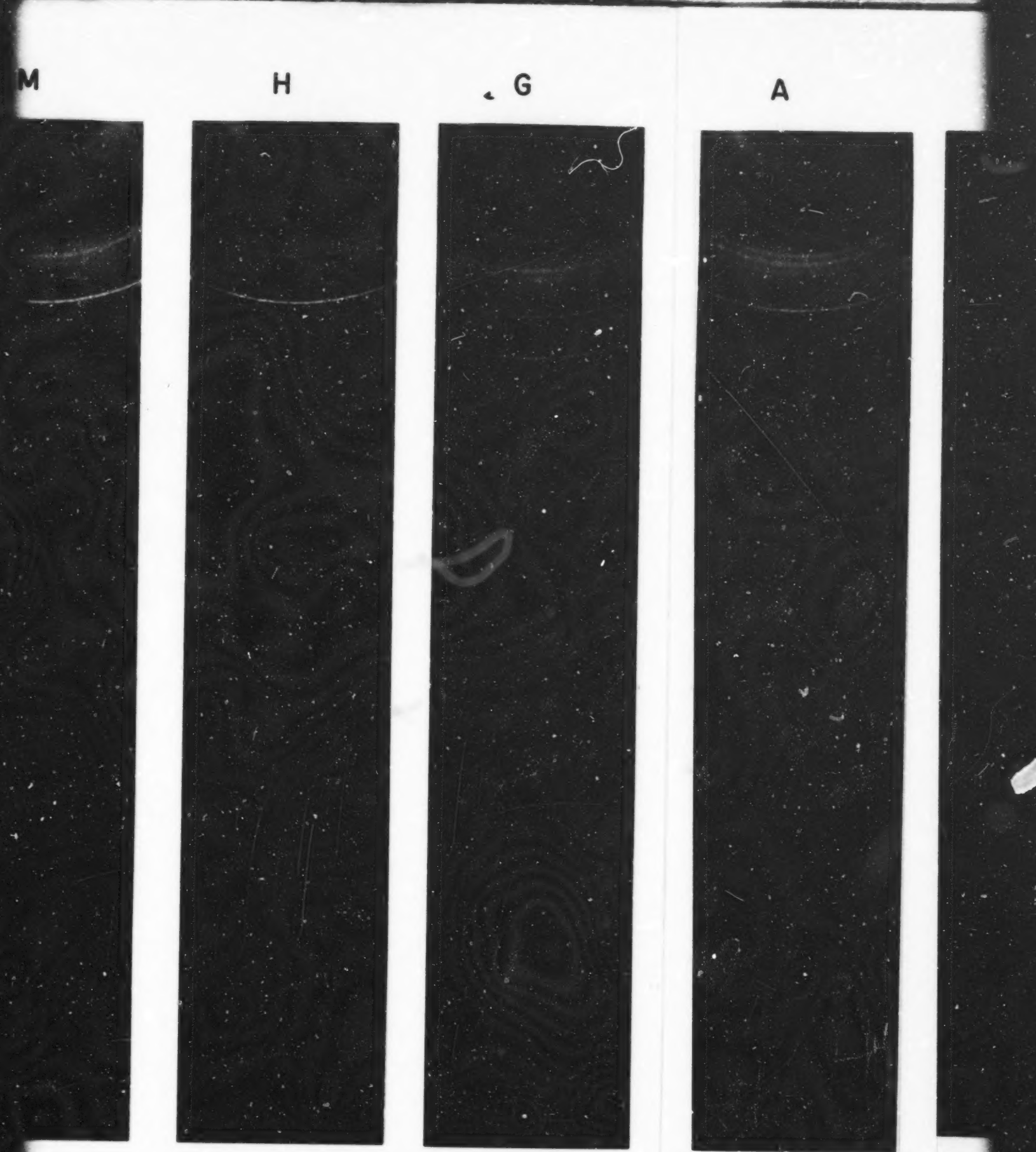
J
L
M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G
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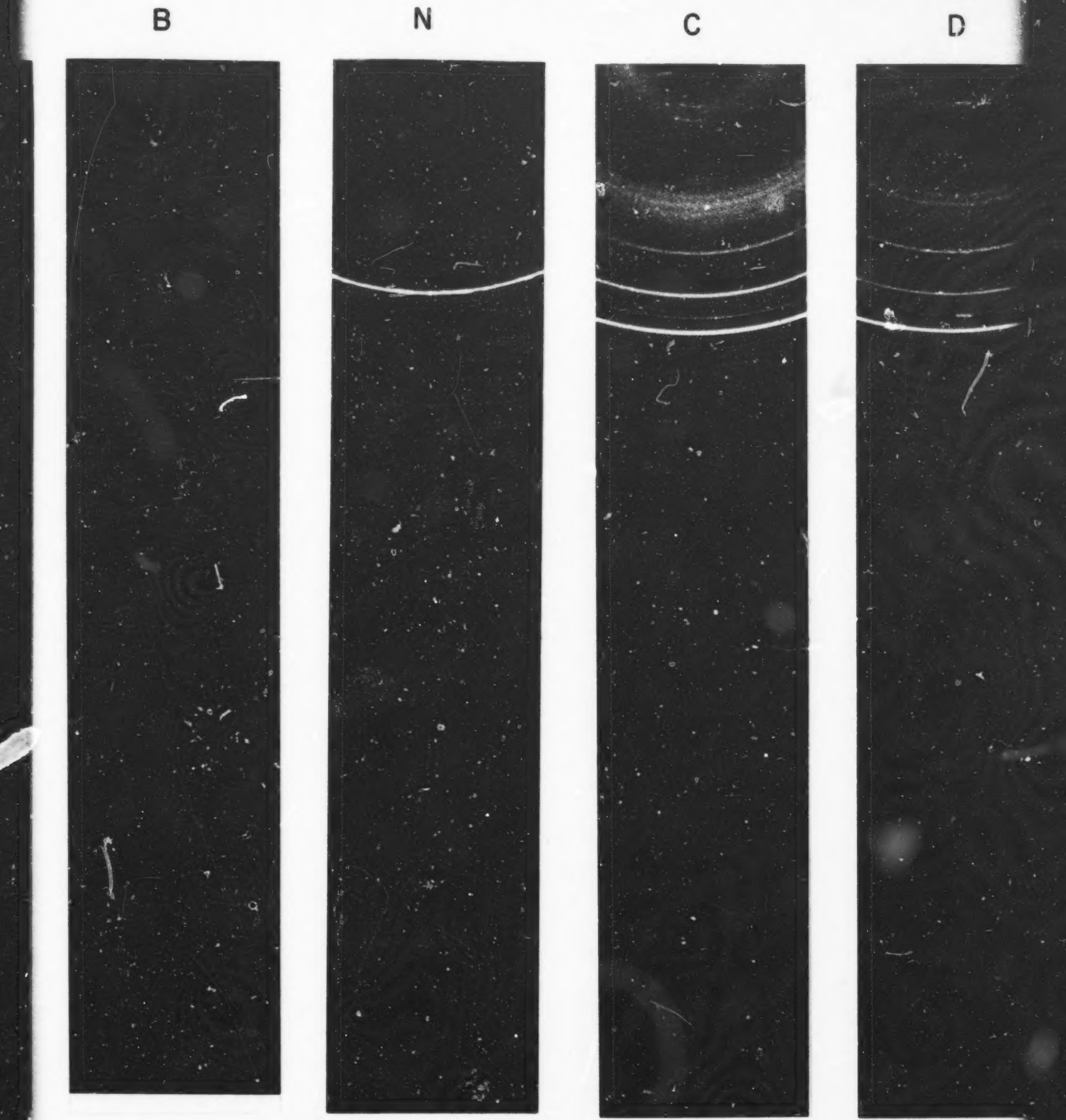
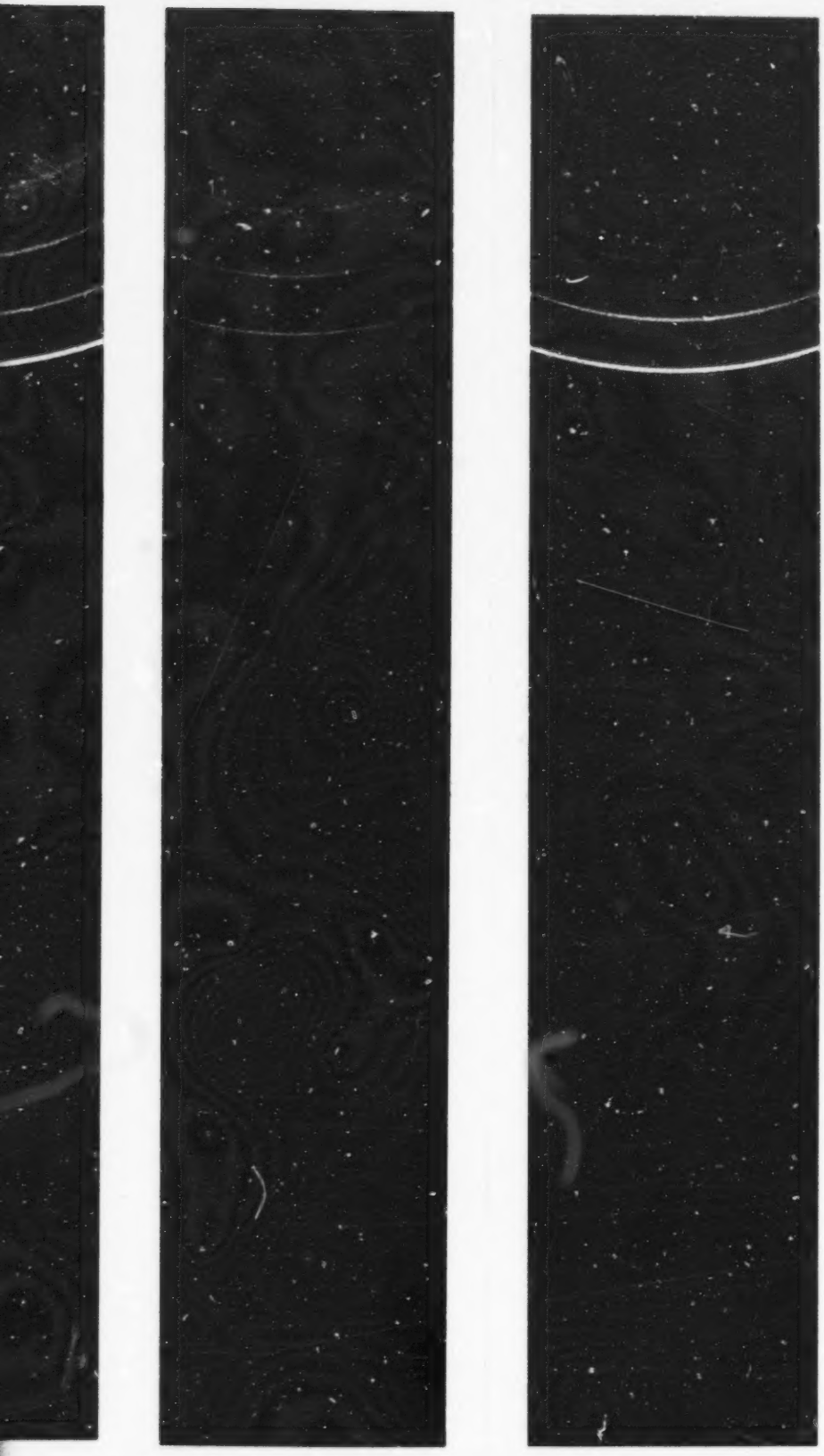

B
N
C
D

E

F



Appendix D

X-ray Data

on

Ashed Filter

Samples